Silver, gold and palladium leaching from electronic scrap using bromine- bromide solution

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Abstract. This study investigated the thermodynamics and kinetics of gold and accompanying noble metals, such as silver, palladium and platinum, leached from the electronic scrap by bromine-bromide solutions. Theoretical and practical analysis of the behavior of gold in the traditional Br_2 - Br^- - H_2O system confirmed the fact that in a neutral and slightly acidic medium, when bromine hydrolysis proceeds slightly, a bromine in bromide solution can be used to leach gold. In this case, bromine-bromide leaching compared with cyanidation is more favorable in terms of kinetics and selectivity. In particular, when brominated in a neutral medium as a result of the formation of a passivating copper monovalent copper (Cu_2O) film on the surface of copper particles, copper does not go into solution, while copper forms stable soluble anionic complexes with cyanide. For the first time in order to stabilize the pH in the alkaline area the conditions for gold leaching in the presence of a phosphate buffer solution (NaH_2PO_4) were investigated. The effect of the pH of the leach solution, the concentration of active bromine, bromide ions and the concentration of the buffer solution on the leaching kinetics of gold was studied. It was established experimentally that a noticeable dissolution of gold begins at pH ≤ 8, and at pH 6, almost all gold passes into the solution. A sufficient concentration of active bromine under these conditions can be considered 6.6 g · dm^{-3} Br_2 at a bromide concentration of 20 g · dm^{-3} NaBr. Leaching with the productive solution turnover made it possible to reduce the consumption of bromine from 89-95 to 20-32 kg Br_2 per ton of scrap and raise the concentration of gold from 76 to 195 mg · dm^{-3}.
In this paper, it was first shown that silver and palladium in the system under study (pH = 5-6) begin to dissolve noticeably only at high concentrations of bromide ions. Complete dissolution of palladium is achieved with an excess of bromide ions and pH values of 1.5-2.0. Platinum turned out to be more resistant to bromine-bromide leaching because of the formation of a sparingly soluble platinum dibromide on its surface.
Key words: gold hydrometallurgy, computer scrap, thermodynamics and kinetics of noble metal dissolution with .bromine, phosphate buffer solution.

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Introduction

Due to the rapid development of technology and an incredible increase in demand for more advanced electronic devices, the service life of the latter is constantly reduced, which causes an increase in the volume of electronic waste. It is generally accepted that electronic waste is a dismantled electrical and electronic equipment due to the expired life and not intended for reuse [1-4, 16-17]. E-waste typically includes household electronic appliances, toys, electrical tools, cell phones, monitoring and control instruments, automatic dispensers, IT, telecom equipment and other consumer items. According to data for 2014, about 41.8 million tons of electronic waste was generated in the world, and it is expected that the

amount of electronic waste will reach 49.8 million tons in 2018, and the annual increase will be from four to five percent [1].

Since e-waste has a high content of copper and precious metals, it is a valuable source of copper for the copper smelters.

The current practice of processing PCB (Personal Computer Boards) concentrates using reflective smelting technology at a smelter does not exclude the loss of precious metals with smelting slags [5,6].

Hydrometallurgical approaches make it possible to eliminate the loss of metals during processing and could be less harmful to the environment once the technology is implemented. Therefore, a combined scheme consisting of enrichment and hydrometallurgical processing of printed circuit boards concentrate seems to be in many respects a technical solution with a high potential [2-4].

The content of non-ferrous and precious metals contained in the final concentrate of printed circuit boards depends on the type of source of the electronic equipment, its composition and especially the year of manufacture. It is well known that the older electronic equipment (60-70 years old) contained significantly more precious metals than modern devices do.

The table. 1 presents the results of the standard chemical analyses of representative samples of PCB concentrates taken from the practice of the Israeli company All Recycling Ltd.

Table 1 - Results of chemical analysis of PCB concentrates

Type	The Results of chemical analysis, vt., %				
	Cu	Ag	Au	Pd	Pt
Rich	17.85	0.126	0.035	0.025	0.0005
Rich	17.51	0.087	0.023	0.017	0.0034
Rich	19.84	0.119	0.031	0.024	-
Reg.	18.19	0.114	0.011	0.010	-
Reg.	18.39	0.136	0.011	0.012	-
Reg.	20.49	0.137	0.006	0.004	0.0003
Poor	26.06	0.052	0.005	0.002	-
Poor	22.46	0.026	0.003	0.002	-

As can be seen from the results of a chemical analysis of ordinary concentrates of printed circuit boards, the general characteristic of PCB concentrates is the multicomponent nature of the raw material, and the content of precious metals varies in the range, wt.,%: Silver (0.026-0.126), gold (0.0034-0.035), palladium (0.0020- 0.025) and platinum (0.00 -0.0034)

Their resistance to oxidative leaching distinguishes gold and platinum group metals.

Oxidation of gold in water proceeds with the sequential formation of monovalent Au (I) and trivalent Au (III) ions, which is confirmed thermodynamically:

$$Au = Au^+ + e \text{-} \varphi = 1.692 + 0.0591 \log [Au^+], \quad (2)$$

$$Au^+ = Au^{+3} + 2e \text{-} \varphi = 1.401 + 0.0295 \log [Au^{3+}]/[Au^+] \quad (3)$$

$$Au = Au^{+3} + 3e \text{-} \quad \varphi = 1.498 + 0.0197 \log [Au^{3+}]; \quad (4)$$

The dissolution of gold can occur only in the presence of a sufficiently strong oxidizing agent, the electrode potential of which is reduced by the introduction of complexing ligands, for example, the bromide ion.

The study evaluated Br2 / Br– system as an alternative to cyanide leaching of gold contained in sulfide and in oxidized concentrates. It was shown [7,8] that when leaching gold contained in sulfide concentrates using elemental bromine, significantly higher gold recovery can be achieved than with cyanide, but the consumption of bromine was high due to the simultaneous oxidation of sulfides. The recovery of gold from oxide concentrates by bromine was comparable to that achievable with cyanide, and bromine consumption was reasonable when leaching was carried out at an almost neutral pH of ~ 6. In the case of oxidized gold-bearing ores containing copper mineralization, bromine consumption was lower than cyanide consumption, as the authors of [7] suggested that bromine with copper minerals is less reactive than cyanide.

As our preliminary experiments with electronic scrap showed, a significant leaching of gold is observed at pH ≥ 8, which allows us to maintain selectivity with respect to the main accompanying metals. In this regard, the study of the optimal conditions for the dissolution of gold and related noble metals in the process of bromine-bromide leaching is of practical and theoretical interest.

Thus, the present work is devoted to studying the thermodynamics and kinetics of the dissolution of gold and related valuable metals, mainly copper, silver, palladium and platinum from typical samples of electronic scrap in the bromine-bromide system, depending on the pH of the medium, the concentration of active bromine, bromide ions and phosphate buffer solution.

Experimental part. Devices and reagents

A series of experiments was prepared using a sample of PCB concentrate composition, vt., %: 20.49 Cu, 5.34 Al, 4.39 Sn, 2.02 Al, 1.39Zn, 3.43 Pb,

1.06 Ni, o.137Ag, 0.0058 Au, 0.0042 Pd, 0.0003 Pt, pre-shredded using a Retch GmbH laboratory hammer shredder to a particle size of 0.5-2 mm.

The reagents used were HCl (Fluka Israel), HNO3 (Fluka Israel), NaBr (Fluka Israel), HBr (Fluka Israel), NaH2PO4 (Fluka Israel) and concentrated (434 $g \cdot dm^{-3}$) elementary bromine solution manufactured by Bromine Compound. Reagent solutions were prepared using bidistilled water.

Leaching was carried out at 298.5 K, the ratio of the contacting phases T: W = 1: 5 and the speed of rotation of the stirrer 300 rpm. $g \cdot dm^{-3}$. The required amount of leaching solution containing 20 $g \cdot dm^{-3}$ NaBr and 70 $g \cdot dm^{-3}$ $NaH_2PO_4 \cdot H_2O$ was poured into a reaction vessel equipped with a mechanical stirrer and electrodes for measuring pH and redox potential (Eh). After that, the required amount of crushed scrap was in reaction vessel uploaded, then the vessel was placed in a Huber GmbH Unistat thermostat and the temperature in the reactor was adjusted to the desired value. Then which the stirrer, measuring instruments were turned on and the pre-calculated amount of concentrated elemental bromine solution (434 $g \cdot dm^{-3}$) was supplied reading recorded original redox - potential, hereinafter in the course of the reaction, adjusting the pH injected 20 $g \cdot dm^{-3}$ NaOH solution if necessary. The gold and copper contents in the solution were analyzed on an ISP-OES instrument. The leach residue was washed, dried, weighed, and the whole sample was decomposed sequentially: first with 6 mol · dm^{-3} with a HNO_3 solution, and then in a solution of aqua regia at 303.5 K, the resulting solutions were analyzed by ISP-OES. Thus, the recovery degree of copper, silver, gold and related platinum group metals was calculated according to the mass balance.

Results and discussion

The Thermodynamics of gold and related metals dissolution in the bromine-bromide system.

The Thermodynamics of the bromine-water system

Bromine is a non-polar hydrophobic compound and its solubility in water is not large, and the following equilibria are observed, as a result of hydrolysis in aqueous solutions (5-7):
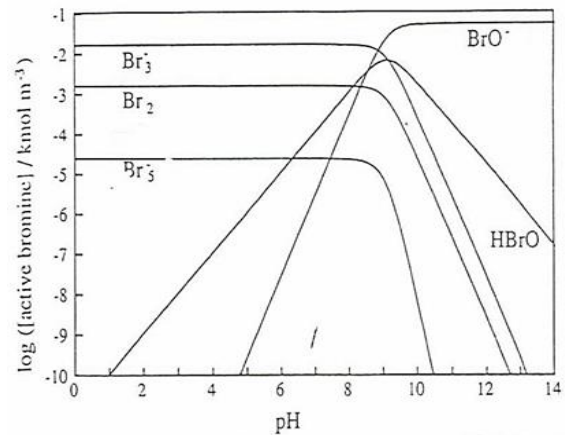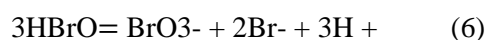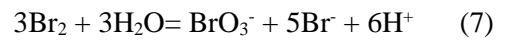
$$Br_2 + H_2O = Br^- + H^+ + HBrO \quad (5)$$

$$3HBrO = BrO3^- + 2Br^- + 3H^+ \quad (6)$$

Fig. 1. The $\log\alpha_{Br2}$ – pH diagram for the bromine – water system at 298K [9].

Thus, the hydrolysis of bromine proceeds according to the equation:

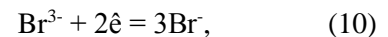$$3Br_2 + 3H_2O = BrO_3^- + 5Br^- + 6H^+ \quad (7)$$

For a stable bromine-water system, Fig. 1 shows that there is a stability region for both bromate (V) and bromate (VII).

At a low bromine content, the bromate (VII) is presented in the form of aqueous particles:

$$Br_{2 \ aq} \leftrightarrow Br_{2 \ (gas)} \quad (8)$$
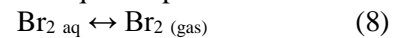
$$\log (Br_{2 \ aq}) = - 0.732 \quad (9)$$

The formation of bromide tri- bromide ions is possible, as an electrochemical process:

$$Br^{3-} + 2\hat{e} = 3Br^-, \quad (10)$$

but it may also be due to a chemical reaction between bromine and bromide

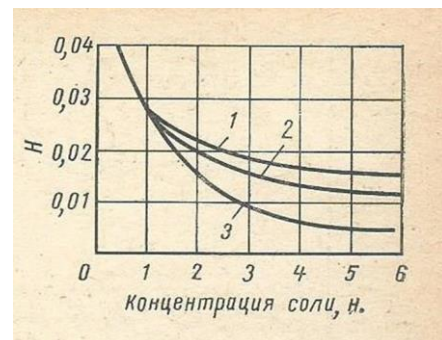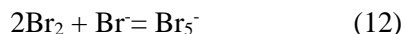$$Br_2 + Br^- = Br_3; \ K = 3.33 \quad (11)$$

Fig. 2. [10] Dependence of the distribution coefficient of bromine H between the gas phase and bromide solutions on their concentration at 298K: 1- NaBr, 2- FeBr₃, 3- NH₄Br

Tri-bromide ions prevail only for bromide activities exceeding 0.89 mol · dm^{-3} Br$^-$. Further addition of a bromine molecule leads to the formation of penta-bromide:

$$2Br_2 + Br^- = Br_5^- \qquad (12)$$

Bromate (I) and bromic (I) acids are not shown in Fig. 3 (Eh-pH diagram), since they are thermodynamically less stable than bromate (V) and bromate (VII).

System Br$_2$ - Br$^-$ - H$_2$O

The bromine distribution between the gas phase and bromide solutions for KBr, NaB, FeBr$_3$, and NH$_4$Br was studied [10]. With an increase in the concentration of bromide ion in water, the solubility of bromine in the bromide medium first rapidly increases, the distribution coefficient decreases accordingly, and then this decrease sharply slows down (Fig. 2). Therefore, in a neutral and slightly acidic environment, where hydrolysis proceeds slightly, a solution of bromine in bromide can be used to dissolve gold.

Au-Br$_2$ - Br$^-$ - H$_2$O system

As can be seen from the Eh-pH diagram [9] (Fig. 3) in the presence of bromide ions, gold dissolves in the form of a tetra-bromo-complex, with the exception of a narrow potential range in which the di-bromo-complex is more stable:
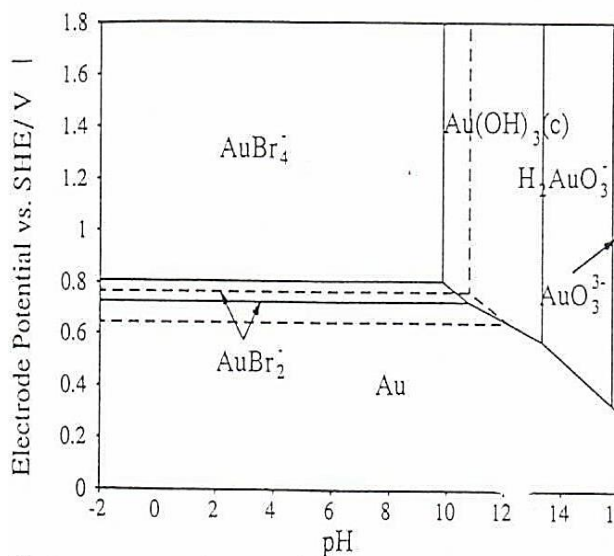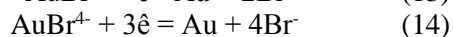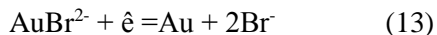
$$AuBr^{2-} + \hat{e} = Au + 2Br^- \qquad (13)$$
$$AuBr^{4-} + 3\hat{e} = Au + 4Br^- \qquad (14)$$

Fig. 3 E-pH diagram for the gold-bromine-bromide system at 298 K and α$_{Au}$ = 1 (____), α$_{Br}$ = 5 (-----); the behavior of the bromide ion is taken without regard to its activity coefficient [9]

Moreover, both bromo-complexes are more stable than the chloride alternatives of the same composition and prevail to a pH of about 9, therefore, according to forecasts, the leaching of gold using bromine can work in a wider pH range than with chlorine.

The disproportionation of di-bromoaurate (I) ions proceeds according to reaction (15):

$$3AuBr_2^- = 2Au + AuBr_4^- + 2Br^- \qquad (15)$$

$3\lg (AuBr_2^-) = -5.25 + \log (AuBr_4^-) + 2 \log (Br^-)$ and has an equilibrium constant of 10–5.25, which indicates that AuBr$_2^-$ ions are more resistant to disproportionation than their chlorine counterparts.

Dadgar A. et all. [11], Pesic B. and Sergent R. [12,13] showed that the kinetics of gold bromination was significantly faster than when gold cyaniding, due to the higher redox potential of the oxidizing agent [13]. The leaching rates of gold from printed circuit boards were at the level of the best cyanidation rates of the computer scrap samples. The study of kinetics using a rotating disk, which was performed by a printed plateau, showed that the bromination reaction is a chemically controlled process [13] at pH <8, above which the leaching rate decreases to zero due to limitations of gold solubility. In the preliminary experiments, we showed that the process of bromination at pH <8, in addition to more favorable kinetics, is distinguished by selectivity, specifically as the copper at bromination process does not go into solution as a result of the formation of a passivating oxide film (Cu$_2$O) on the surface of copper particles while with cyanide copper forms stable water-soluble anionic complexes.

However, the dissolution of gold in the Br$_2$- Br$^-$ - H$_2$O system with the formation of anionic gold bromide complexes is accompanied by hydrolysis of the total reaction:

$$Au + Br_2 + 2Br^- + H_2O = AuBr_4^- + HBrO + H^+ \qquad (16)$$

which causes acidification of the medium and a pH shift towards the formation of soluble copper bromide compounds, which is accompanied by a decrease in the concentration of active bromine. We have studied the process of gold dissolution in the bromine-bromide system in the presence of a phosphate buffer solution (NaH$_2$PO$_4$) to constantly maintain the pH at a given level. In the table. Figures 2–4 present experimental data on the kinetics of gold leaching from pre-ground (–0.5–2 mm) samples of PCB concentrate with varying pH values from 8 to 6.16.

Table 2 Kinetics of gold leaching in bromine - bromide system at pH 8.0

Duration, min	Solution of Br_2, ml	$[Br_2]$, gr·dm^{-3}	Eh, мB	pH	Solution of NaOH, ml	E_{Au}, %	E_{Cu}, %
0	2	1.4	878	7.91	1.5	-	-
10	4	3.1	884	7.89	1.6	-	-
20	6	2.8	882	7.86	1.8	2.4	-
30	8	3.6	883	7.90	1.8	3.5	-
40	10	3.6	881	7.85	1.8	4.5	1.4
60	11	3.4	880	8.06	1.9	4.8	1.2
80	12	3.2	880	7.84	1.9	5.2	1.1
90	13	3.0	890	7.70	1.9	5.9	0.6
110	14	2.8	889	7.91	2.0	4.6	0.6
120	14	2.8	887	7.93	2.1	3.8	0.4
180	14	2.8	887	7.77	2.2	3.6	0.2
Solid loss of gold, %					96.4		

Table 3 Kinetics of gold leaching in bromine - bromide system at pH 7.00

Duration, min	Solution of Br_2, ml	$[Br_2]$, gr·dm^{-3}	Eh, мB	pH	Solution of NaOH, ml	E_{Au}, %	E_{Cu}, %
0	1	1.6	893	7.01	1.2	-	-
10	2	3.5	896	7.01	1.3	12.6	-
20	3	3.6	888	7.04	1.3	22.1	-
30	4	3.9	902	7.05	1.4	34.7	2.3
40	5	4.0	896	7.03	1.5	46.7	2.6
60	6	3.6	897	7.01	1.5	53.8	1.8
80	6	3.6	897	6.98	1.5	55.3	1.8
90	6	3.1	896	6.99	1.5	68.2	1.6
110	6	3.1	896	6.99	1.5	72.4	1.4
120	7	2.9	896	6.99	1.5	77.8	1.2
180	11	2.6	894		1.5	84.4	1.2
Solid loss of gold, %					14.4		

Table 4 Kinetics of gold leaching in bromine - bromide system at pH 6.16

Duration, min	Solution of Br_2, ml	$[Br_2]$, gr·dm^{-3}	Eh, мВ	pH	Solution of NaOH, ml	E_{Au}, %	E_{Cu}, %
0	2	1.8	894	6.16	-	-	-
10	4	4.4	905	6.11	-	16.4	-
20	6	5.2	908	6.12	-	27.4	2.6
30	8	6.1	911	6.14	-	36.2	2.8
40	10	4.9	912	6.12	1	48.2	3.2
60	11	5.2	910	6.20	1	56.7	3.4
80	12	5.8	910	6.16	1	66.4	3.6
90	13	6.1	910	6.12	1	69.8	3.8
110	14	6.6	907	6.09	1	75.9	4.4
120	14	6.4	907	6.06	1	88.7	4.2
180	14	6.1	907	6.12	1	98.9	4.0
Solid loss of gold, %				1.0			

As can be seen from the data presented in table. 2-4, a noticeable leaching of gold in the Br_2-$NaBr$-$NaOH$-$NaH_2PO_4 \cdot H_2O$ system begins at pH <8 and at pH 6 almost all the gold goes into solution. A sufficient concentration of active bromine in solution for the successful oxidative leaching of gold under these conditions can be considered 6.6 g · dm^{-3} Br_2 at a concentration of bromide of 20 g · dm^{-3} NaBr.

The increased bromine consumption at pH 8.0 and 6.0 observed in the experiments occurs in the first case due to hydrolysis by reactions (5–7) with the formation of very weak oxidizing agents BrO^{3-} (V) and BrO^{4-} (VII) bromates [9], and in the second case the concentration of bromine decreases as a result of the associated oxidation of copper and related metals. It should be noted that by the method of x-ray phase analysis it was found that if at pH 8 copper is oxidized on the surface to a dense film of copper (I) oxide resistant to dissolution, then at pH 6 grains of poorly soluble CuO and $CuBr_2$ appear along with the bulk of brown cuprite $Cu_2O \cdot 3Cu (OH)_2$.

In Tables 5 and 6 there is the experimental data on the effect of a buffer solution concentration in the range of 30–50 g·dm^{-3} $NaH_2PO_4 \cdot H_2O$ on the kinetics of gold and copper leaching at a concentration of 20 g·dm^{-3}NaBr bromide.

Table 5 Kinetics of gold leaching in the bromine - bromide system at an initial pH of 5.5, the volume of a solution of bromine 20 ml and30 g dm^{-3} $NaH_2PO_4 \cdot H_2O$

Duration, min	$[Br_2]$,gr·dm^{-3}	Eh, мВ	pH	Solution NaOH , ml	E_{Au}, %	E_{Cu}, %
0	32.60	901	5.50	0.4	-	-
20	30.40	893	5.15	0.8	45.20	2.8
40	25.98	891	4.75	1.6	74.08	3.4
60	23.50	888	4.80	3.6	82.76	3.6
80	23.00	886	5.22	5.5	88.74	4.2
90	22.50	885	5.15	6.2	97.52	4.6

Table 6 Kinetics of gold leaching in a bromine - bromide system at an initial pH of 5.2, a volume of a solution of bromine of 20 ml and a concentration of $NaH_2PO_4 \cdot H_2O$ equal to 50 $g \cdot dm^{-3}$

Duration, min	$[Br_2]$, $gr \cdot dm^{-3}$	Eh, мВ	pH	Solution NaOH , Σ ml	E_{Au}, %	E_{Cu}, %
0	32.80	895	5.27	0.2	-	-
20	33.52	895	5.12	0.4	62.43	2.4
40	28.84	896	5.20	0.8	92.53	2.8
60	25.48	897	5.16	0.8	96.40	3.0
80	24.53	896	5.08	0.8	96.20	3.4
90	22.86	896	5.07	0.8	96.60	3.8

Looking at the experimental data presented in table 5 and 6, we can conclude that an increase in the concentration of the buffer solution significantly reduces the consumption of alkali to maintain a given pH. In addition, it was noted that a higher content of $NaH_2PO_4 \cdot H_2O$ in the leach solution slightly reduces the transfer of copper to the solution, and an X-ray phase analysis of the leach residue made it possible to identify CuH_2PO_4 grains in the washed scrap along with Cu_2O, CuO and $AgBr$. In the next series of experiments, we studied the effect of the concentration of active bromine (Br_2) on the rate and complreteness of gold leaching and the behavior of copper at a concentration of 20 $g \cdot dm^{-3}$ NaBr bromide. The obtained experimental data is summarized in the tables 7 and 8.

Table 7 Kinetics of gold leaching in the bromine - bromide system at an initial pH of 5.0, a bromine solution volume of 10 ml and 60 $g \cdot dm^{-3}$ $NaH_2PO_4 \cdot H2O$

Duration, min	$[Br_2]$, $gr \cdot dm^{-3}$	Eh, мВ	pH	Solution NaOH , ml	E_{Au}, %	E_{Cu}, %
0	14.26	916	5.03	0.1	-	-
20	14.22	908	5.34	1.0	69.43	1.4
40	12.84	892	5.67	4.5	81.23	1.8
60	10.48	891	5.06	4.7	95.43	2.0
90	9.93	889	5.18	5.4	97.20	3.4
120	7.73	860	5.55	10.6	96.74	3.6
160	3.50	860	5.60	12.2	96.10	3.2
180	5.95	860	5.60	20.2	89.26	1.8

Table 8 Kinetics of gold leaching in a bromine - bromide system at an initial pH of 5.2, a volume of a solution of bromine of 20 ml and 60 $g \cdot dm^{-3}$ $NaH2PO4 \cdot H_2O$

Duration, min	$[Br_2]$, $gr \cdot dm^{-3}$	Eh, мВ	pH	Solution NaOH , мл	E_{Au}, %	E_{Cu}, %
0	34.26	895	5.27	0.4	-	-
20	33.64	896	5.12	0.4	62.43	2.6
40	28.84	882	5.20	0.8	92.53	2.8
60	26.48	898	5.16	1.4	96.43	3.0
80	24.66	896	5.08	1.4	96.20	3.4
90	22.74	894	5.07	1.6	97.60	4.6

As can be seen from the data presented in table 7 and 8, a change in the initial concentration of active bromine in the range of 14.26–34.26 g·dm⁻³ Br₂ upon leaching for 0–90 min does not significantly affect the rate and the degree of the gold recovery. With an increase in the duration of leaching, when the bulk of the gold acts as a protective layer, has gone into solution and almost the entire surface of copper contact networks becomes open, the concentration of active bromine drops sharply and the kinetic dependence of the degree of leaching of gold passes through a maximum and begins to decrease. Intensive oxidation of copper is accompanied by acidification of the medium and increased consumption of alkaline solution for pH correction.

It should be noted that, judging by the results of laboratory experiments, the amount of bromine consumed in the leaching process was 89-95 kg Br₂ per ton of scrap. In order to reduce bromine consumption and find new ways to concentrate gold, the leaching process with the circulation of the productive solution was studied, and the concentration of active bromine was allowed to be adjusted by discrete supply of calculated quantities of a solution of 435 g·dm⁻³ Br₂ and a buffer solution of 60 g·dm⁻³ NaH₂PO₄·H2O .

In the table. 9 shows the experimental data of countercurrent leaching of 7 representative samples of a regular PCB concentrate, previously ground to a particle size of 0.5-2 mm, the duration of each stage is 160 minutes. In the first stage, a solution was used after leaching a representative sample of a regular PCB concentrate under standard conditions with an initial concentration of active bromine of 34.26 g·dm⁻³ Br₂.The results are shown in table 9 show that by turning the productive solution over five leaching stages, it is possible to increase the gold concentration by 3.5 times from 44 to 152 ppm. In this case, the degree of transition of gold into solution falls within acceptable limits from 98.23 to76.58%. We can assume that if leaching is carried out in

countercurrent, then the completeness of extraction and a high degree of gold concentration can be maintained. At the same time, it should be noted that through the use of a reverse leach solution for dissolving gold from five samples of regular PCB scrap, even with correction of the active bromine concentration, it was possible to reduce the oxidizer consumption from 89-95 to 20-32 kg Br₂ per ton of scrap.

Silver, palladium and platinum in the bromine-bromide system

As mentioned earlier, the electronic scrap is a complex raw material of precious metals and, in addition to gold, contains industrially significant concentrations of platinum group metals, especially palladium. In the process of gold leaching in a productive solution, in addition to gold (52 ppm), traces of iron (3.4 ppm) and copper (6-8 ppm) were found. Silver, palladium and platinum in the solution were not detected. Silver was previously detected in the leaching residue in the form of metal inclusions coated on the surface with a dense AgBr film, which is easily formed under conditions of gold leaching by the reaction:

$$Ag + Br^- = AgBr + ê, \qquad (17)$$
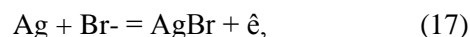
which is thermodynamically expressed by equation (18)

$$\varphi = 0.03 - 0.0591 \lg [Br^-] \qquad (18)$$

Chemical analysis of the solid residue after bromine-bromide leaching of gold from palladium-rich PCB scrap showed the content in it, vt., %: 17.34 Cu, 4.18 Al, 5.16 Sn, 1.83 Fe, 2.26 Zn, 4.18 Pb, 0.520 Ag, 0.00003 Au, 0.036 Pd and 0.0005 Pt. In this sample, the search experiments were carried out (Tables 10-12) to study the conditions for the extraction of silver, palladium and platinum in the bromine-bromide system.

Table 9 The results of gold leaching in the bromine - bromide system at an initial pH of 5.1 with a phase ratio T: W = 3: 1 with a turnover of the productive solution

Stage	[Br₂] start	[Br₂] end	Br, ml	NaOH, ml	Buffer solution, ml	Eh, мB	pH	[Au], Ppm start	[Au], Ppm end	EAu, %
I	34.26	22.5	-	1.6	-	894	5.1	44	76	98.23
II	13.72	18.7	1.6	2.3	19.2	911	5.8	68	112	92.56
III	16.8	12.5	2.4	3.4	32.4	897	6.3	100	140	87.30
IV	10.4	11.6	3.2	3.8	58.6	901	5.2	128	164	81.65
V	7.9	10.2	4.0	4.2	68.9	899	5.8	152	195	76.58

**Table 10** Kinetics of leaching of silver and palladium in the bromine - bromide system at an initial pH of 6.0, the volume of bromine solution is 14 ml, the phase ratio T: W = 1: 3 and the concentration of bromide ions is 103.5 $g \cdot dm^{-3}$

Duration, min	[Br$_2$], gr·dm^{-3}	Solution NaOH , Σ ml	Eh, мB	pH	E$_{Ag}$, %	E$_{Pd}$, %
0	23.20	2.0	879	6.0		
60	23.10	2.0	876	5.8	14.15	6.23
240	22.84	2.2	874	5.9	26.72	12.10
300	22.43	2.4	874	5.9	34.15	17.82
360	22.28	2.4	874	5.8	48.92	29.15ê
900	22.13	2.4	877	5.8	82.35	61.66

Table 11 Kinetics of leaching of silver and palladium in the bromine - bromide system at an initial pH of 1.98, a bromine solution volume of 16 ml, a phase ratio of T: W = 1: 5 and a concentration of bromide ions of 100.5 $g \cdot dm^{-3}$

Duration, min	[Br$_2$], gr·dm^{-3}	Solution HBr(62%) , Σ ml	Eh, мB	pH	E$_{Ag}$, %	E$_{Pd}$, %
0	29.86	0.2	879	1.98		
60	26.10	0,2	846	1.50	38.62	16.83
240	22.84	0.3	834	1.50	53.25	38.16
300	18.43	0.8	812	1.50	72.62	57.82
360	22.28	2.4	774	1.50	92.37	79.15
900	22.13	2.4	784	1.50	95.62	93.20

The experimental results showed that at pH 6, silver and palladium begin to dissolve only at a high concentration of bromide ions. In this case, 82.35% silver and only 61.66% palladium can be converted into a solution. To transfer all palladium into a solution, the pH must be shifted to the acidic region to pH 1.98-1.5. Silver is quite completely dissolved in a wide range of pH1.5-6.0. The results obtained are in good agreement with the well-known fact that hardly soluble silver (I) halide in the presence of an excess of halide ions forms soluble highly charged anionic complexes [14, 15]. For AgBr, this can be described by the following reactions:

$$AgBr + Br^- = AgBr2^- \qquad (19)$$

$$AgBr_2^- + Br^- = AgBr_3^{2-} \qquad (20)$$

In the case of palladium, it is known that its oxidation, for example, with nitric acid, in the presence of bromide ions results in the formation of a brown mass of PdBr2, which is hardly soluble in aqueous medium, but soluble in hydrobromic acid [15]. As can be seen from the experiments, the dissolution of palladium with the formation of the anionic complex of palladium (II) PdBr42- can be described, thermodynamically very likely, by reaction (21):

$$Pd + Br_2 + 2Br^- \leftrightarrow PdBr_4^{2-} + 2ê, \qquad (21)$$
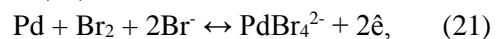
$$\varphi = 0.49 + 0.0296 \log [PdBr_4^{2-}] - 0.0296$$
$$\log P_{Br2} -0.0591 \log [Br^-]$$

Dependent on the concentration of bromide ions. However, in practice, the process proceeds

slowly, since it is passivated by the formation on the surface of particles of palladium dibomide -$PdBr_2$, which is hardly soluble at pH 5-7, and therefore, the dissolution is practically not completed. In the presence of hydrobromic acid (pH 1.98) and an excess of bromide ions, judging by the leaching duration, the process is also accompanied by the formation of a palladium dibromide film, which then dissolves in the acid.

As can be seen from the data given in table. 15 and 16, the dissolution of palladium in the bromine-bromide system proceeds much more slowly in comparison with the behavior of gold. When the medium is acidified with hydrobromic acid and all other things being equal, the recovery of palladium increases from 61.66 to 93.20%. However, if at pH 6.0 only 11 ppm of copper was found in the productive solution, then the acid solution contains, $g \cdot dm^{-3}$: 0.0105 Pd, 0.56 Pb, 2.6 Ag, 11.3 Cu. Thus, it was found that at pH 1.98 it was possible to transfer the main amount of palladium and silver into the solution, however, about 20% of the copper passed into the solution. It was not possible to trace the behavior of platinum under the conditions of bromine-bromide leaching of the presented PCB samples, due to its extremely low content.

Thus, it has been experimentally shown that bromine-bromide leaching allows selective and high-speed recovery of gold from electron scrap in an alkaline medium and is an effective alternative to direct cyanidation. The leaching conditions of silver and palladium in the bromine-bromide system are practically presented and theoretically justified. It was shown that during the bromine-bromide leaching in an alkaline medium, the dissolution of copper is impeded by the formation of a passivating film of hardly soluble oxide (Cu_2O) on its surface. However, when silver and palladium are leached, up to 20% of copper is dissolved with a slightly acid bromine-bromide solution, and iron, aluminum, zinc and tin pass into the solution simultaneously. The dissolution of related metals, especially copper, causes an increased consumption of bromine and complicates the practical use of the technology. Therefore, in further work, the conditions of the joint bromine-bromide leaching of silver, gold, and palladium after preliminary leaching of the accompanying metals and copper from the initial PCB concentrate were investigated.

Findings. A noticeable dissolution of gold in the bromine-bromide system begins at pH≤8, and at pH = 6 almost all of the gold passes into the solution quite selectively. A sufficient concentration of active bromine under these conditions can be considered 6.6 $g \cdot dm^{-3}$ Br_2 at a bromide concentration of 20 $g \cdot dm^{-3}$ NaBr.

Leaching with recirculation of the productive solution allowed to reduce the consumption of bromine from 89-95 to 20-32 kg Br_2 per tonne of scrap and to increase the concentration of gold from 76 to 195 $mg \cdot dm^{-3}$.

It was shown for the first time that silver and palladium in the studied system (pH = 5-6) can be dissolved only at high concentrations of bromide ions. Complete dissolution of palladium is achieved at a concentration of bromide ions of 100.5 $g \cdot dm^{-3}$ and pH = 1.5-2.0.

The high efficiency of bromine-bromide leaching allows further development of thr research in the direction of leaching of precious metals in one stage in a slightly acidic medium after preliminary leaching of copper and related metals.

Бром-бромид жүйесінен алтын, күміс, палладий, платинаны электрондық сынықтардан шаймалау

Коган В. С., Беркович И. В.

Түйіндеме. Электрондық сынықтардан бром- бромид ерітінділерінің, алтын және ілеспе асыл металдардың, мысалы күміс, палладий мен платина сияқты шаймалау термодинамикасы мен кинетикасы зерттелді. Дәстүрлі Br₂ - Br⁻ - H₂O жүйесіндегі алтынның көрсететін қасиеттерін теориялық және практикалық талдап, бейтарап және әлсіз қышқылдық ортада бромның гидролизі біршама төмен жүретінін және бромидтегі бром ерітіндісін алтынды шаймалау үшін қолдануға болатындығын дәлелдеді. Сонымен қатар, бром- бромидті шаймалау цианизациямен салыстырғанда анағұрлым қолайлы кинетикасы және селективтілігімен ерекшеленеді. Атап айтқанда, мыс бөлшектерінің бетінде бір валентті мыс оксидінің (Cu₂O) пассивті пленкасының пайда болуы нәтижесінде бейтарап ортада бромдау мыс ерітідіге өтпейді, ал мыс цианидпен тұрақты еритін анион комплекстерін құрайды. Сілтілік ортадағы рН мәндерін тұрақтандыру үшін фосфатты буферлік ерітінді (NaH₂PO₄) кезіндегі алтынды шаймалау шарттары алғаш рет зерттелді. Активті бром, бромид иондарының концентрациясы және буферлі ерітінді концентрациясының шаймалау ерітіндісіндегі рН мәні, алтынның шаймалау кинетикасына әсері зерттелді. Эксперименталды түрде алтынның айтарлықтай еруі рН ≤ 8-ден бастап, рН 6-да барлық алтын ерітідіге түсетіні анықталды. Осы жағдайларда белсенді бромның жеткілікті концентрациясын 6,6 гд⁻³ Br₂, NaBr бромидтің концентрациясы 20 гДм⁻³ деп санауға болады. Өнімді ерітіндіні циркуляциялау арқылы шаймалау бромды тұтынудың бір тоннасы үшін 89-95-тен 20-32 кг Br2 азайтуға және алтынның концентрациясын 76-дан 195 мг·дм⁻³-ке дейін арттыруға мүмкіндік берді. Жұмыста алғаш рет, қарастырылып отырған күміс пен палладий жүйесіндегі (рН = 5-6) бромид иондарының жоғары концентрациясында ғана айтарлықтай ери бастайтыны зерттелген. Палладийдің толық еруі 100 г·дм-3 ион бромидінде және рН = 1,98 деңгейінде болды.

Түйін сөздер: алтын гидрометаллургиясы, компьютерлік сынықтар, броммен асыл металдардың еруі термодинамикасы мен кинетикасы, фосфатты буферлік ерітінді.

Выщелачивание золота, серебра, палладия и платины из электронного скрапа в бром-бромидной системе

Коган В. С., Беркович И. В.

Аннотация. Изучена термодинамика и кинетика выщелачивания золота и сопутствующих благородных металлов, таких как серебро, палладий и платина, из электронного скрапа бром-бромидными растворами. Теоретический и практический анализ поведения золота в традиционной системе Br₂ – Br⁻ - H₂O подтвердил факт, что в нейтральной и слабокислой среде, когда гидролиз брома протекает незначительно, раствор брома в бромиде можно использовать для выщелачивания золота. При этом бром-бромидное выщелачивание по сравнению с цианированием отличается более выгодной кинетикой и избирательностью. В частности, медь при бромировании в нейтральной среде в результате формирования на поверхности частичек меди пассивирующей пленки оксида одновалентной меди (Cu₂O), не переходит в раствор, в то время, как с цианидом медь образует устойчивые растворимые анионные комплексы. С целью стабилизации значений рН в щелочной области впервые исследованы условия выщелачивания золота в присутствии фосфатного буферного раствора (NaH₂PO₄). Изучено влияние на кинетику выщелачивания золота рН выщелачивающего раствора, концентрации активного брома, бромид-ионов и концентрации буферного раствора. Экспериментально установлено, что заметное растворение золота начинается при рН≤ 8, а при рН 6 в раствор переходит практически все золото. Достаточной концентрацией активного брома в этих условиях можно считать 6.6 г·дм⁻³ Br₂ при концентрации бромида 20 г·дм⁻³ NaBr. Выщелачивание с рециркуляцией продуктивного раствора позволило снизить расход брома с 89-95 до 20-2 кг Br₂ на тонну скрапа и поднять концентрацию золота с 76 до 195 мг·дм⁻³. В работе впервые показано, что серебро и палладий в изучаемой системе (рН=5-6) начинают заметно растворяться только при высоких концентрациях бромид-ионов. Полное растворение палладия было достигнуто при 100 г·дм⁻³ бромид ионов и значениях рН=1.98.

Ключевые слова: гидрометаллургия золота, компьютерный скрап, термодинамика и кинетика растворения благородных металлов бромом, фосфатный буферный раствор.

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